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THE ABSOLUTE VALUE OF AN ELECTRODE POTENTIAL

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THE ABSOLUTE VALUE OF AN ELECTRODE POTENTIAL

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HISTORICAL AND INTRODUCTORY

The method of determining the difference of potential between two electrodes dipping into a common electrolyte is a relatively simple and an extremely accurate one. When, however, attempts have been made to determine the difference of potential existing between a single electrode and an electrolyte, difficulties were encountered, and the results which were obtained were far from concordant.

There are four principal lines of attack on the problem of determining the absolute value of an electrode potential, namely, the dropping electrode, the capillary electrometer, endosmosis phenomena and electrostatic differences of potential.

The dropping electrode and the capillary electrometer were developed shortly after Helmholtz[1] enunciated his theory of the so-called "electrical double layer." In this theory it was assumed that when an electrode is placed in an electrolyte of the proper concentration, there is immediately set up a charge of one sign on the electrode and a charge of the opposite sign on the electrolyte. It was thermodynamically shown that when the magnitude of these charges was at a minimum the surface tension of a liquid metal electrode, such as mercury, was at a maximum.

Acting on this theory, Lippman[2] in 1875, measured the surface tension of mercury in contact with sulfuric acid solutions of different concentrations, and at that concentration at which the surface tension was at a maximum, he assumed that the difference of potential was zero, that is, that the electrical double layer did not exist. Conversely, if we impose a potential upon mercury in contact with a sulfuric acid solution, of such a magnitude and opposite in sign to that resident upon the mercury, as to cause the surface tension to increase to a maximum, this is the magnitude of the potential resident upon the mercury because of the electrical double layer.

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1. Wied. Ann. 7; 340.
2. Compt. Rend. 83; 192: 95; 686.
   Ann. Chem. Phys. 5; 532.

By a somewhat similar line of reasoning, it was thought that a mass of mercury placed in contact with a calomel solution and a second connection made by means of an electrode, the surface of which was changing so rapidly that the electrical double layer could not form, should give the potential of massive mercury against its salt solution.

The two methods described above gave for the absolute potential of the normal calomel electrode, +0.593 volts. The positive sign indicates that the mercury was more positive than its salt solution.

The next work on the subject of absolute potential measurement was done by Billitzer[3] in 1903. He observed the behavior of minute metallic particles and fine platinum wires suspended in solutions of different concentrations when acted upon by an electrical field. He reasoned that when the concentration of the solution was such that the fine particles in the one case and the platinum wires in the other did not move under the influence of an electrical field, the particle or wire was at a zero potential with respect to the solution. In other words, this was the iso-electric point. From this work, he showed the absolute potential of a normal calomel electrode to be —0.125 volts. This indicates that the electrode is about 0.7 volts more negative than the generally accepted value obtained by the dropping electrode and the capillary electrometer. Billitzer says that this is due to the dependence of the surface tension upon the applied E. M. F., the maximum surface tension appearing when the electrode is about 0.7 volts negative to the solution.

Ewell[4], working by electrostatic methods found the absolute potential of a metal electrode to be about 0.5 volts more negative with respect to its solution than is the value given by the capillary electrometer. He states that increasing the concentration of the salt solution seems to decrease the potential, that is, that the effect is the opposite of that to be expected from Nernst's theory.

Various experimenters who have found it necessary to use reference electrodes have, after critical examination, con-

3. Zeit. fur Elekt. Chem. 12; 192: 8; 638.
4. Phys. Rev. 6; 271.

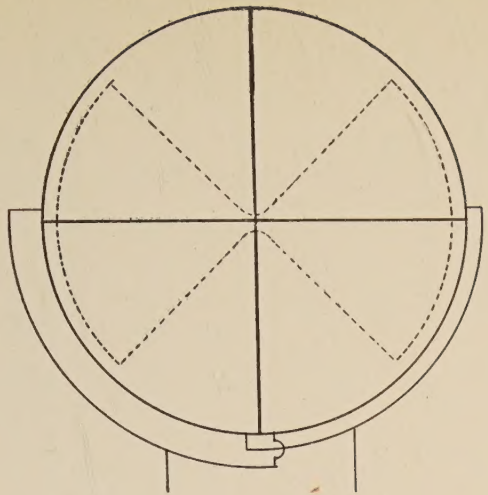

Fig 1

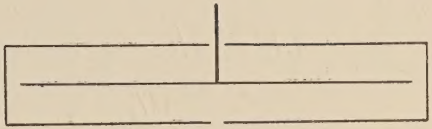

Fig 2

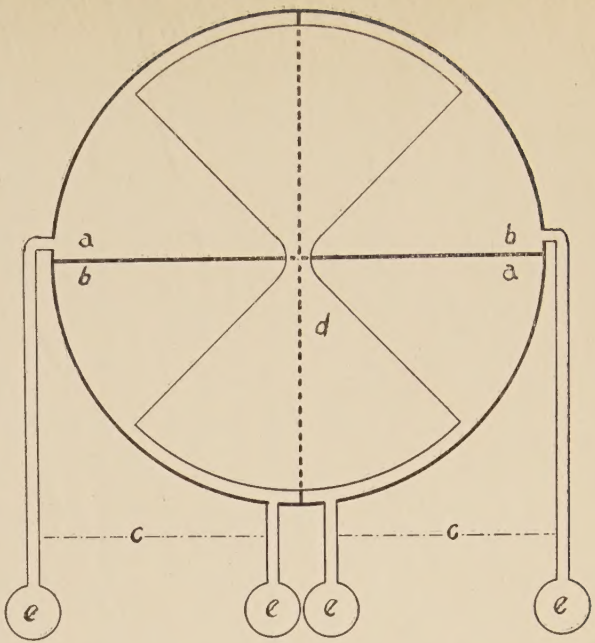

Fig 3

Plate I

cluded that the value for the potential of the calomel electrode as given by the dropping electrode and the capillary electrometer is in error. This, together with the fact that endosmosis methods and the electrostatic method give results at wide variance from the accepted value, indicates the necessity for further research along this line.

Dr. H. P. Cady and Mr. E. F. Stimpson commenced work on the present method of measurement of absolute potentials in 1903, but due to the illness of Mr. Stimpson, the work was discontinued and not taken up again till the fall of 1921, when Mr. George Lynn started working on the problem.

Mr. Lynn built an electrometer of the same general type as that used in the present work, and with this secured results, which as he says, "are not clear cut in their indications," but which demonstrated the practicability of the method, and indicated that instead of being positive with respect to a normal Potassium Chloride-Calomel solution, mercury was probably negative.

The work was taken up by the author and an electrometer built which differed from that of Mr. Lynn's in that his was of the co-axial needle type, while that used in the present work was of the plane needle type. By this modification, it was possible to have no solid dielectric between the needle and the quadrants, and at the same time not introduce serious complications in the method of operation.

DESCRIPTION OF THE INSTRUMENT

The quadrant electrometer consists of four hollow metal quadrants produced by cutting a hollow cylinder by two mutually perpendicular planes intersecting along the axis of the cylinder. Inside this is the needle, shaped in the general form of two opposite quadrants. This needle is made of any light conducting material and is suspended by means of an electrically conducting filament. The quadrant and needle system is shown diagramatically and in section in figures 1 and 2 respectively on Plate I.

Now if each pair of opposite quadrants are electrically connected, and are insulated from the other pair of quadrants and a charge of electricity placed upon the needle,

which is placed symmetrical with respect to a diameter, it can be seen that any difference of potential existing between the quadrants will produce an electrostatic attraction of the needle by one pair of the quadrants and a repulsion by the other pair. The magnitude of this movement can be shown to be nearly proportional to the difference of potential between the pairs of quadrants, provided the needle potential is kept constant. The needle would place itself entirely inside the pair of oppositely charged quadrants were it not for the restoring effect of the suspension. Thus we have two opposite effects; the deflecting couple, produced by the electrostatic difference of potential, and the restoring couple of the suspension.

The amount of deflection caused by a difference of potential of one volt across the pairs of quadrants when the needle is charged to any given potential is a measure of the sensitivity of the instrument at that potential.

The instrument which was built for this work was a modification of the conventional quadrant electrometer. The metal quadrants were replaced by quadrant-shaped glass cups (a, a) and (b, b), each of which was connected with a glass tube syphon system (c), which terminated in a well (e), as shown in figure 3 on Plate I.

The quadrants (a, a) were filled with mercury, as were the syphon tubes and wells in connection, and the quadrants (b, b) were filled with salt solution in contact through the syphon tubes with mercury and calomel paste in the wells. The mercury quadrants were connected through a potentiometer circuit to the mercury in contact with the salt solution in the other quadrants. This gave us a half cell built in the electrometer itself. Provision was made for raising and lowering the needle (d) and for rotating it through small angles. Now it can be seen that if a difference of potential existed between the mercury which filled quadrants (a, a) and the solution which filled quadrants (b, b) its magnitude could be known if the sensitivity of the electrometer were known, and the direction of the movement of needle would clearly indicate the sign of the charge upon the mercury or upon the solution.

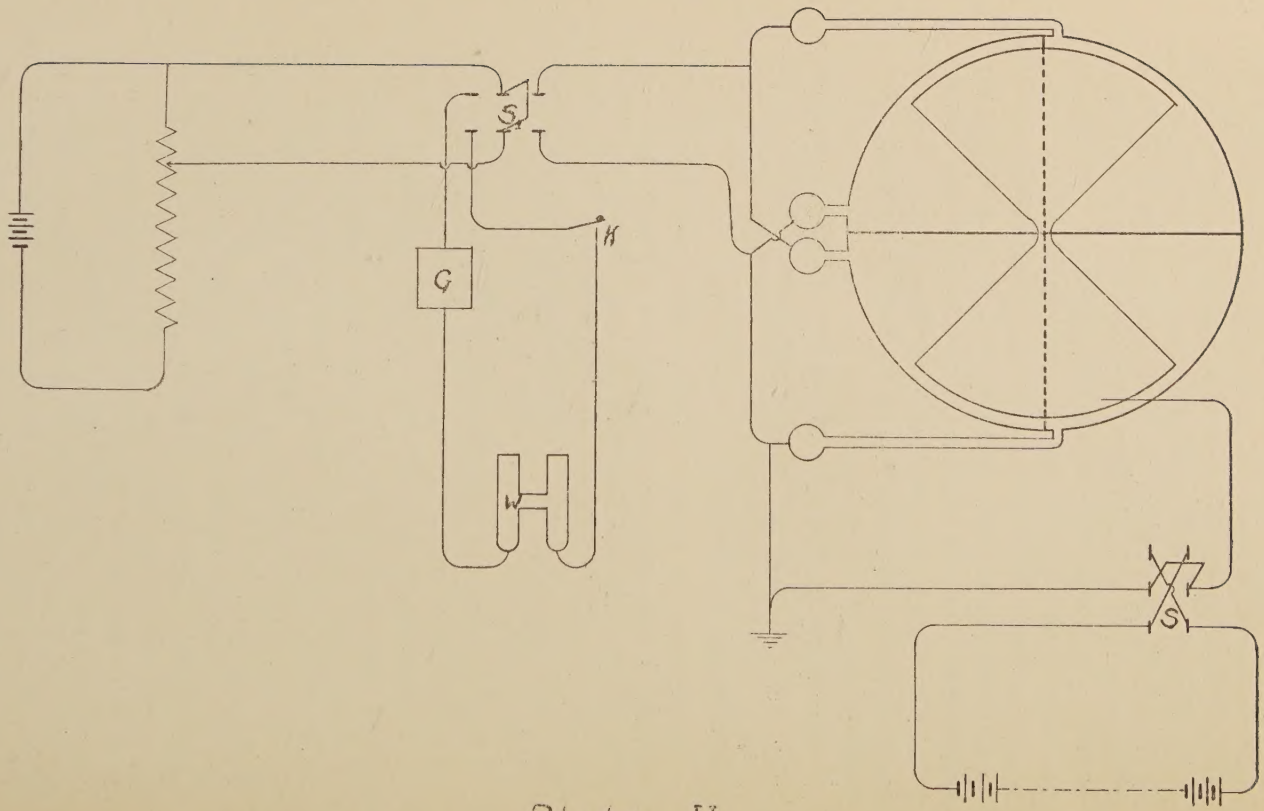

Plate II

The instrument was mounted upon a block of lead weighing 100 pounds, which in turn rested upon small rods set in the foundation. This foundation went to bed rock. This arrangement stabilized the instrument against horizontal displacement. The case of the electrometer was earthed, as were the quadrants which were permanently filled with mercury. Surrounding the electrometer was a metal box which was also earthed to shield out any external electrical fields. Lead-in wires were passed into the metal box through sulfur insulators. The potentiometer was mounted on a separate table on a dry pine board which was insulated from the table by sulfur blocks. The needle charging battery of dry cells, of a potential of 225 volts, was similarly mounted. The telescope and scale were mounted on a wall shelf at a distance of three meters from the electrometer.

Connections with the needle charging battery and the potentiometer are shown in the diagram, Plate II. The switch (S) is a reversing switch for changing the sign of the potential on the needle. (S_1) is a switch for connecting the standard cell (W) and the galvanometer (G) or the quadrant electrometer in the potentiometer circuit. (K) is a key for closing the galvanometer circuit.

The sensitivity of the electrometer was determined by filling all the quadrants with mercury and applying a known difference of potential across them, the needle potential being varied between 25 and 225 volts. It was found that the maximum sensitivity compatible with stability was secured with a potential of 155 volts on the needle. The sensitivity thus obtained was 132 millimeters per volt. This seemed sufficient for our purpose.

EXPERIMENTAL

In the early experimental work of this investigation, the sensitivity of the electrometer was determined by filling both pairs of quadrants with mercury and ascertaining the deflection caused by a known potential across the quadrants. Then while leaving the needle potential the same, the mercury was drawn off from one pair of quadrants and solution substituted, thus giving a complete half cell. From the

deflection produced by the half cell and the known sensitivity of the instrument, attempts were made to compute the E. M. F. of the half cell. Difficulty was met with in getting the level of the solution exactly the same as the level of the mercury when the sensitivity of the electrometer was determined, so this method gave very erratic results and the method of operation was changed. The method next tried was to earth the needle, and when it had come to rest, read its zero position. Then a potential was placed on the needle and a counter E. M. F. of sufficient magnitude placed across the quadrants in the proper sense to return the needle to its zero position. This should be the potential of the half cell.

The undesirable feature in this method was that the rapid movement of the needle when charged, caused currents in the air inside the electrometer case, which were in some instances several hours in dying out.

The last, and most successful method used was to connect the quadrants through the potentiometer circuit, but have a zero potential across the quadrants from the potentiometer circuit, that is, the only potential on the quadrants was the potential of the half cell. With the needle charged, its position was read by means of the telescope and scale. The sign of the needle potential was then changed, but the magnitude kept constant. This of course caused the needle to be deflected in the opposite direction. Now sufficient E. M. F. from the potentiometer circuit was placed across the half cell to bring the needle to the position which it had before the sign of the needle potential was changed. This was twice the potential of the single electrode.

Under these conditions, there were of course currents of air set up in the electrometer case which were slow in dying out. However, this was eliminated as soon as the E. M. F. of the half cell was approximately known, as it was possible to reverse the sign of the needle potential and at the same time set the potentiometer to that potential which prevented deflection except for a very small amount, which was compensated for in the final adjustment of the potentiometer.

This method proved quite satisfactory. There were, however, other difficulties which prevented the results from

being reliable at first. Electrical effects due to the passing of street cars were without difficulty shielded to earth, but a stray electrical effect made the results erratic for weeks in spite of every effort to locate the source. It was finally found that the wind blowing against a window near the electrometer was causing the trouble. When the glass was washed with a solution of calcium chloride and earthed this difficulty was removed.

A more detailed description of the manipulations of securing a reading follows.

The mercury in one set of quadrants was drained off and the quadrants filled with tenth normal Potassium Chloride-Calomel solution. Mercury and calomel paste were placed in the wells in contact with the solution.

The needle was charged at a positive potential and the scale read with no potential on the quadrants other than the potential of the half cell itself. The sign of the potential on the needle was reversed and sufficient E. M. F. applied to the quadrants to restore the needle to the position which it had occupied when positively charged. Half of this potential would prevent the deflection of the needle when the sign of the needle potential was changed, so is the potential of the half cell. In order to use this method, it was necessary to have the needle exactly symmetrical with respect to the quadrants[5] and the quadrant surfaces at the same height. If the first point was neglected, half the potential as indicated above would not keep the needle at zero position when the sign of the needle potential was reversed. The accurate leveling of the conducting quadrant surfaces was necessary only to secure maximum sensitivity.

When the quadrants were filled with tenth normal Potassium Chloride-Calomel solution, it was found that the positively charged needle was deflected from its zero position toward the mercury-filled quadrants, and on reversing the sign of the needle potential, was deflected toward the solution-filled quadrants. This clearly indicates the negative character of the mercury with respect to its salt solution.

5. Phys. Rev. 13; 228.

The potential necessary to be placed across the quadrants to restore the needle to the position which it had before the sign of the needle potential was reversed was —0.634 volts. The negative sign indicates that the mercury was negative with respect to the solution. After each day's work the instrument was torn down and the quadrants, syphon tubes and wells thoroughly cleaned. The instrument was then rebuilt and the quadrants refilled for the next day's readings. It was possible to secure about fifteen readings per day.

The results given below are the counter E. M. F.'s necessary to restore the needs to the position which it had before reversal of the sign of the needle potential. The readings for any single day are more concordant than are the means for the different days. No reason can be given for this, as the experimental conditions were duplicated as exactly as possible.

Each column of data given below is the readings taken during one day when the tenth normal calomel electrode was used.

—0.683	—0.650	—0.660	—0.661	—0.630
—0.683	—0.650	—0.660	—0.660	—0.631
—0.690	—0.650	—0.658	—0.660	—0.631
—0.685	—0.650	—0.656	—0.660	—0.652
—0.686	—0.650	—0.602	—0.661	—0.660
—0.685	—0.650	—0.661	—0.658	—0.620
—0.685	—0.650	—0.658	—0.660	—0.621
—0.685	—0.651	—0.662	—0.660	—0.621
—0.684	—0.650	—0.660	—0.660	—0.621
—0.685	—0.650	—0.661	—0.660	—0.621
—0.683	—0.651	—0.658	—0.661	—0.621
—0.684	—0.650	—0.660	—0.660	—0.621
	—0.651	—0.660		
	—0.651	—0.660		
	—0.650			

—0.682	—0.683	—0.565	—0.535	—0.645	—0.660
—0.677	—0.685	—0.565	—0.544	—0.660	—0.660
—0.680	—0.685	—0.565	—0.594	—0.664	—0.659
—0.679	—0.685	—0.564	—0.595	—0.660	—0.662
—0.680	—0.685	—0.531	—0.593	—0.661	—0.656
—0.680	—0.685	—0.565	—0.594	—0.662	—0.657
—0.680	—0.685	—0.532	—0.594	—0.664	—0.661
—0.680	—0.685	—0.576	—0.542	—0.661	—0.660
—0.679		—0.598	—0.551	—0.660	—0.659
—0.681		—0.608	—0.542	—0.658	
—0.679		—0.608	—0.546		

The mean double E. M. F. for the tenth normal electrode was —0.634 volts, which would give as the potential of the single electrode —0.317 volts.

Similar data for the normal calomel electrode follow:

—0.686	—0.735	—0.686	—0.700	—0.724
—0.688	—0.740	—0.684	—0.700	—0.730
—0.690	—0.729	—0.686	—0.700	—0.724
—0.688	—0.730	—0.686	—0.702	—0.726
—0.710	—0.730	—0.688	—0.700	—0.772
—0.708	—0.730	—0.692	—0.721	—0.769
—0.710	—0.726	—0.691	—0.720	—0.770
—0.700	—0.729	—0.691	—0.718	—0.770
—0.700	—0.729	—0.691	—0.720	—0.770
—0.700	—0.730	—0.690	—0.720	—0.770
—0.700	—0.730	—0.690	—0.722	—0.769
—0.700		—0.690	—0.720	—0.771
—0.700		—0.692	—0.720	
—0.702		—0.691	—0.720	
—0.699		—0.692		
—0.700		—0.692		

—0.701	—0.700	—0.730	—0.800
—0.700	—0.700	—0.746	—0.800
—0.698	—0.700	—0.729	—0.800
—0.700	—0.700	—0.765	—0.802
—0.699	—0.698		—0.800

—0.699	—0.801
—0.700	—0.800
—0.693	

The average double value here is —0.730 volts, so the potential of the normal half cell is —0.365 volts.

It will be observed that the difference of potential between the normal and the tenth normal half cell is 0.048 volts, which is very close to the value to be computed from the ion concentration by the Nernst formula.

After these data were taken, the calomel cell was replaced by the electrode Hg||HgO—NaOH. After allowing the half cell to stand for three days to come to constant potential, the potential was determined in the same manner as for the calomel electrode.

For the tenth normal basic half cell, the following data were taken:

—0.761	—0.759	—0.765	—0.763
—0.760	—0.759	—0.766	—0.762
—0.764	—0.760	—0.766	—0.763
—0.760	—0.761	—0.784	
—0.760			

The average double value here is —0.762 volts or the E. M. F. of the single electrode is —0.381 volts. Here again the mercury is negative with respect to the solution.

Using the normal basic half cell the following data were obtained:

—0.895	—0.879	—0.900	—0.880	—0.886
—0.897	—0.876	—0.888	—0.890	—0.886
—0.885	—0.890	—0.881	—0.891	—0.885
	—0.881			—0.884
	—0.882			

The average for these values gave for the potential of the normal basic half cell, —0.444 volts.

The difference of potential of 0.079 for the cell

+Hg|N/1 KCl-Hg_2Cl_2||N/1 NaOH-HgO|Hg—

does not agree well with the value 0.1541 volts[6] which is

6. Tables Annuelles de Constants et Donnees Numeriques 1911.

obtained by the potentiometer method. Applying the correction for the difference of potential between the solutions does not entirely correct this discrepancy. The difference of potential between the normal and tenth normal basic half cells is closely in keeping with that to be expected from cells of this type.

CONCLUSIONS

From this work it appears that mercury, instead of being positive with respect to its normal and tenth normal KCl-Hg_2Cl_2 and NaOH-HgO solutions, is in fact negative. Our reference electrodes give a potential about 0.92 volts more negative than the values which are at present accepted.

We must therefore conclude that the value of +0.61 volts for the deci-normal and +0.56 for the normal calomel electrodes which are given by the dropping electrode and the capillary electrometer are not the electrostatic differences of potential existing between the metal and the solution, and that at the condition of maximum surface tension for mercury, the mercury and solution are not iso-electric.

ACKNOWLEDGMENT

The writer wishes to state again that the fundamental idea underlying this investigation was Dr. Cady's, and to thank Dr. Cady for his helpful supervision and timely suggestions throughout the work.

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*A very extensive bibliography on the subject of absolute potential measurement is attached to this article.

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